Life cycle assessment of nanocomposites made of thermally conductive graphite nanoplatelets

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Abstract

Purpose Polymers typically have intrinsic thermal conductivity much lower than other materials. Enhancement of this property may be obtained by the addition of conductive fillers. Nanofillers are preferred to traditional ones, due to their low percolation threshold resulting from their high aspect ratio. Beyond these considerations, it is imperative that the development of such new fillers takes place in a safe and sustainable manner. A conventional life cycle assessment (LCA) has been conducted on epoxy-based composites, filled with graphite nanoplatelets (GnP). In particular, this study focuses on energy requirements for the production of such composites, in order to stress environmental hot spots and primary energy of GnP production process (nano-wastes and nanoparticles emissions are not included).

Methods A cradle-to-grave approach has been employed for this assessment, in an attributional modeling perspective. The data for the LCA have been gathered from both laboratory data and bibliographic references. A technical LCA software package, SimaPro (SimaPro 7.3), which contains Ecoinvent (2010) life cycle inventory (LCI) database, has been used for the life cycle impact assessment (LCIA), studying 13 midpoint indicators. Sensitivity and uncertainty analyses have also been performed.

Results and discussion One kilogram of GnP filler requires 1,879 MJ of primary energy while the preparation of 1 kg of epoxy composite loaded with 0.058 kg of GnP 303 MJ.

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Besides energy consumption in the filler preparation, it is shown that the thermoset matrix material has also a non-negligible impact on the life cycle despite the use of GnP: the primary energy required to make epoxy resin is 187 MJ, i.e., 62 % of the total energy to make 1 kg of composite.

Conclusions Raw material extraction and filler and resin preparation phase exhibit the highest environmental impact while the composite production is negligible. Thermosetting resin remains the highest primary energy demand when used as matrix for GnP fillers. The result of the sensitivity analysis carried out on the electricity mix used during the GnP and the composite production processes does not affect the conclusions.

1 Introduction

Epoxy resins, through their chemical and electrical resistances, are used for adhesives, protective coating, embedding, casting, and composites, in electrotechnical industry (Kočí and Loubal 2012).

Polymers typically have intrinsic thermal conductivity much lower than those for metals or ceramic materials. A typical value for epoxy material thermal conductivity is 0.19 W/mK. The thermal conductivity of polymers has been traditionally enhanced by the addition of thermally conductive fillers, including among others graphite and carbon nanotubes (Ebadi-Dehaghani and Nazempour 2012; Harris 2004). Many applications would benefit from the use of polymers with enhanced thermal conductivity. When used as heat sinks in electric or electronic systems, composites with a thermal conductivity approximately from 1 to 30 W/mK are required

(King et al. 1999). Epoxy resins as nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the filler phase. The area of the interface between the matrix and filler phase is typically an order of magnitude greater than that for conventional composite materials; therefore, a relatively small amount of nanoscale filler can have an observable effect on the macroscale properties of the composite. Carbon-based fillers are the most promising fillers, due to their high thermal conductivity and lightweight. Enhancement of thermal conductivity by 100 % for only 1 wt% of multi-walled carbon nanotube (MWCNT) or GnP loading is achieved which is not attainable with conventional micronic fillers (Balandin 2011). Obtaining composites having thermal conductivities higher than 4 W/mK and usual polymer processability is however very challenging (Han and Fina 2011). On the one hand, natural graphite is still abundant and is of lower cost compared to the other nanosize carbon materials. Actually, the cost of producing graphite nanoplatelets is expected to be ~$11/kg (~$5/lb) (Ebadi-Dehaghani and Nazempour 2012). On the other hand, worldwide commercial interest in carbon nanotubes is reflected in a production capacity that presently exceeds several thousand tons per year (De Volder et al. 2013). Currently, bulk purified MWCNT are sold for less than $100 per kilogram, which is still 1- to 10-fold greater than commercially available carbon fiber. The high cost of carbon nanotubes (CNTs) is inhibiting broad-based industrial applications. GnP may be potential substitutes for CNTs in nanocomposites due to their lower price (Fukushima et al. 2006; Segal 2009).

In addition to these aspects, it is necessary to take into account the environmental impact profile of GnP nanocomposites. There is an increasing concern in the environmental aspects associated with nanoproducts. Investigations are requested in order to avoid unintended consequences (Upadhyayula et al. 2012) and to make correct decisions concerning the manufacturing, use, and disposal of these products.

This paper is intended to focus on the impact assessment of epoxy nanocomposite life cycle. The aim of the life cycle assessment (LCA) presented in this paper is therefore to obtain the potential energy and impacts of epoxy resins filled with GnP.

2 Methods

The approach taken in this paper is the attributional approach. Attributional LCA (ALCA) provides information about the impacts of the processes used to produce, and consume and dispose of a product, but does not consider indirect effects arising from changes in the output of a product (Brander et al. 2009). In particular, it uses average data; it is based on stoichiometric relationships between input and outputs, and the

results are produced with known levels of accuracy. This study has been conducted in accordance with ISO14044. A commercial LCA software package, SimaPro (SimaPro 7.3), which contains Ecoinvent (2010) life cycle inventory (LCI) database for commercially available and processing technologies, has been used for the life cycle impact assessment. Thirteen environmental mid-points indicators have been studied according to Hassanzadeh et al. (2012) (Table 1). In particular, life cycle energy estimates are made using the cumulative energy demand (CED). With this method, energies are provided in terms of total quantity of primary energy and resources needed for the entire value chain. Moreover, the Intergovernmental Panel on Climate Change Global Warming Potential (IPCC GWP) method which lists the climate change factors of IPCC with a time frame of 100 years and provides emissions in terms of kilogram CO_2 equivalents is used. The methods and indicators carried out are reported in Table 1.

In order to define the functional unit used in this study, a practical use of epoxy nanocomposites has been considered. Thermal interface materials (TIMs) are commonly required to facilitate the transfer of thermal energy from electronic components to a heat sink. Heat dissipation from electronic components is an increasingly important problem because of the rapid growth of high-performance, high-power computer processing units (Balandin 2011). Commercial TIMs are typically based on composites of polymers which are filled with thermally conductive particles (Haddon et al. 2010).
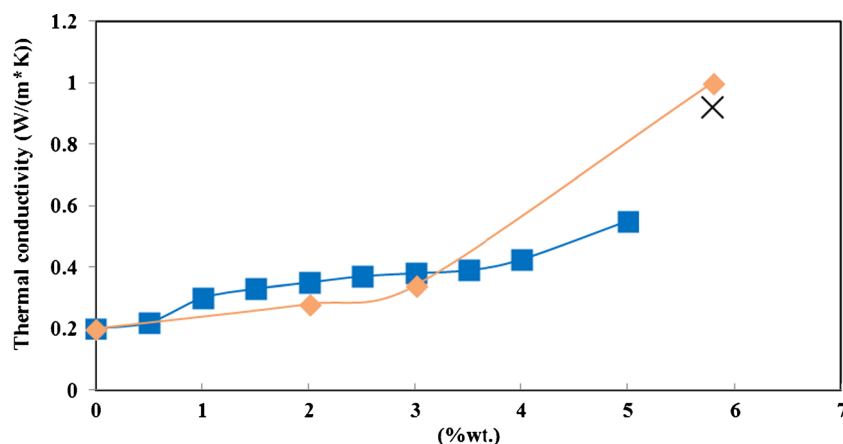
Table 1 Optimized methodology for life cycle assessment under SimaPro 7.3.0

Optimized methodology

Indicators	Methodology	Unit
Metal depletion	ReCiPe midpoint (H)	kg Fe eq.
Fossil depletion	ReCiPe midpoint (H)	kg Oil eq.
Energy consumption	Cumulative Energy Demand	MJ primary
Water depletion	ReCiPe midpoint (H)	m^3
GWP 100a	IPCC 07	kg CO_2 eq.
Ozone depletion	CML 2001	kg CFC-11 eq.
Human toxicity	USEtox	Cases
Ecotoxicity	USEtox	PAF m^3 day
Photochemical oxidant	ReCiPe midpoint (H)	kg NMCOV eq.
Acidification	CML 2001	kg SO_2 eq.
Fresh water Eutrophication	ReCiPe midpoint (H)	kg P eq.
Marine Eutrophication	ReCiPe midpoint (H)	kg N eq.
Hazardous waste	EDIP 2003	kg

Cases are numbers of persons affected by the life cycle product. PAF m^3 day indicates potentially affected fraction of species (PAF) integrated over time and volume

NMVOC non-methane volatile organic compounds

Fig. 1 Enhancement of thermal conductivity with raw GnP_M fillers (*square*), GnP obtained after strong and long ultrasonication treatments (Shahill and Balandin 2012, losange and Yu et al. 2008, cross) (GnP_M stands for powders made of platelets of 6-nm-thick and 25-μm large. The platelets are rather thick with about 20 layers of graphene in comparison with the data reported by Shahill)

Consequently, all calculations are made for a functional unit defined as the complete life cycle of 1 kg of epoxy composite with 5.8 wt% of filler assuring a thermal conductivity of 1 W/mK and a lifetime of 30 years. Figure 1 depicts thermal conductivity versus filler amount for GnP. The objective is to perform a complete life cycle assessment for epoxy GnP composite processes in the goal to obtain epoxy nanocomposites with high thermal conductivity. A 1 W/mK is already 400 % higher than the value of conductivity obtained with pristine epoxy (0.2 W/mK).

2.1 Data quality and collection

This paper presents an LCA conducted directly on a laboratory-scale process for the production of high-quality epoxy nanocomposite. The system boundaries of this study represent a cradle-to-grave perspective, i.e., from the extraction of the various resources used in the production of such an epoxy composite to the final disposal at the end of life of such a product. Figure 2 shows all the stages taken into account in the life cycle of GnP epoxy composite, included in a
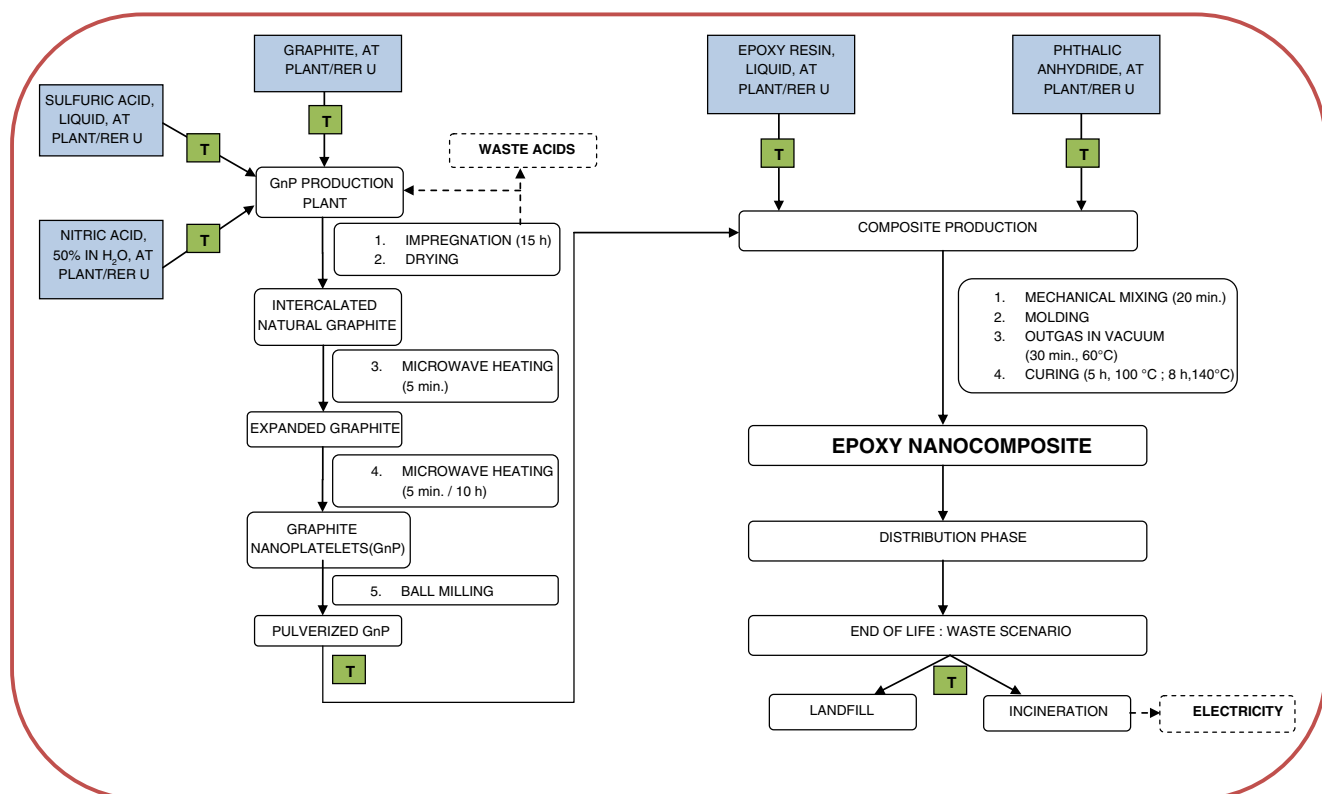

Fig. 2 Life cycle system boundary, from cradle to grave, considered for the LCA of GnP epoxy nanocomposite. Elements that have not been considered are indicated by *dashed lines*, and transport stages are reported with *T squares*

continuous line boundary. Various techniques have been employed to collect data along the life cycle of this product. Both laboratory data and bibliographic references were considered. Transport stages are included in the assessment. According to Hassanzadeh et al. (2013), in case of unavailability of transport data, penalizing average data were established and used in this LCA. Modification of transportation data marginally modifies the impact assessment. A distance of 19,000 km was considered for world boat transport and a transport default scenario of 1,000 km for local truck >32 t. According to the attributional modeling, the Union for the Coordination of Transmission of Electricity (UCTE) mix has been used as default. For sensitivity analysis, the Swiss electricity mix was considered. Furthermore, epoxy resin is not considered to contribute to an increased environmental load during the use phase. As a consequence, this phase has not been considered in the life cycle impact assessment (LCIA). Other assumptions taken in order to complete the assessments are reported in the LCI description for the different phases.

2.2 Life cycle inventory—description of GnP production process

The graphite nanoplatelet (GnP) is an emerging class of nanomaterials. A GnP is a nanoscale platelet composed of several layers of a graphene plane, with a platelet thickness of less than 2 to 15 nm. Few graphene layers sheets represent a robust and compelling alternative to single-layer graphene in the fabrication of advanced composites (Haddon et al. 2010).

The purpose of the following description is to show the mechanism of the GnP production process considered in this LCA.

The starting material is graphite. Individual molecular layers of graphite are held together with weak Van der Waals forces (5.1 kJ/mol between two layers separated by 0.336 nm (Dresselhaus and Dresselhaus 2002)). This separation energy provides an estimate for the potential barrier that must be overcome when an intercalate layer is introduced into the graphite host. Many chemical species have been used to intercalate graphite materials. The type of graphite intercalation compound considered in this study is the *sulfate* intercalation. This material is manufactured by treating highly crystalline natural flake graphite with a mixture of sulfuric acid and an oxidizing agent, the nitric acid, which aid in *catalysis* of the sulfate intercalation http:// asbury.com/technical-presentations-papers/materials-in-depth/ expandable-flake-graphite/. In particular, in order to prepare SO_3-graphite interlayer compound, according to Kwon et al. (2001), it has been considered that natural granular graphite was treated with an acid mixture of sulfuric acid 95 % and nitric acid 62 %. The graphite was exposed to the acid mixture for 15 h at about room temperature. The graphite intercalated compound (GIC) is then filtered to substantially remove the excess of acid, washed with distilled water, and dried prior to

further processing in order to remove water remaining within the graphite. With this conventional intercalation method, graphite particles are impregnated with a large amount of concentrated acid mixture for a prolonged period of time. As a consequence, the consuming amount of the acid mixture is very large. In this study, the system boundary does not include the large amount of waste acid generated by this phase, so not considering the complicated treatment task of the waste acid in order to recover it for further applications. A novel method for producing expanded graphite using a single oxidant such as fuming sulfuric acid or anhydrous sulfuric acid, minimizing the amount of the consuming acid and hazardous waste acids and so providing a recycling step of the sulfuric acid, was implemented by Kwon et al. (2001). The primary reason for *sulfate* intercalation is to impart the ability of the treated flake graphite to exfoliate, or expand when heated. High temperature causes the acid trapped between the graphene layers to gasify, producing enough pressure to push adjacent graphite layers apart. In fact, the actual cause of expansion/ exfoliation is the increase in volume, and resultant pressure, caused by rapid heating of the intercalant, that is converted from a liquid phase to a gas phase. Gas formation results in an increase in volume of the intercalant of approximately 1,000 fold. The pressure generated by this volume increase forces the adjacent graphene layers to separate, resulting in an accordion expansion http://asbury.com/technical-presentations-papers/materials-in-depth/expandable-flake-graphite/. These materials are not completely exfoliated and contain extensive domains of stacked graphitic layers. The maximum expansion potential of a specific grade of intercalated graphite can only be realized if the heating rate used to affect exfoliation is rapid. Since the expansion process depends on harnessing the force developed by an expanding gas, it is important to develop maximum force by causing a sudden, rapid gas expansion http://asbury.com/ technical-presentations-papers/materials-in-depth/expandable-flake-graphite/. In this study, according to Drazl and Fukushima (2009), it has been considered a microwave expansion as a fast and economical method to expand chemically intercalated graphite flakes. Microwave energy at 2.45 GHz for 5 min is carried out to GIC. This technique does not in itself lead to individual GnP, however. This is due to the domains of retained graphite spacing which result in non-uniform expansion in the *c*-axis. A further step of microwave heating results in the need to physically break the expanded worm-like graphite. According to Li and Zhong (2011) and Haddon et al. (2010), it was considered that in order to obtain stable dispersion of graphite nanoplatelets and to avoid the re-aggregation of the sheets due to the flexible nature of the graphite, subsequent application of microwave was expected from a few minutes to several hours. In particular, according to Blake et al. (2008), a period of 3 h was assumed. The expanded, exfoliated graphite can then be pulverized by ball milling to produce graphite flakes platelets with high aspect ratio, which are suitable starting materials for the fabrication of advanced composites. It is worth to note that recent works show that the

strong oxidizers such as sulfuric and nitric acid oxidize graphite. This results in the introduction of oxygen containing functional groups such as hydroxyl and epoxide. The evolved gases that cause the rapid expansion are found to be only carbon dioxide and water suggesting that the gaseous products are derived from the exothermic decomposition of hydroxyl and epoxide groups, not the vaporization of intercalated species (McAllister et al. 2007). Figure 3 depicts all the production steps, while Table 2 resumes the main data assumptions for the GnP production process, concerning both stoichiometric mass flows and energy requirements, in order to satisfy the functional unit. Further inventory data concerning the raw materials extraction and preparation are not reported, as they are already included in the Ecoinvent modules used in this study.

2.3 Life cycle inventory—production of epoxy nanocomposite

The production of the epoxy nanocomposite involves different steps. Specifically, the preparation of thermosetting composite polymers starts from dispersing the filler and adding the curing agent (phthalic anhydride) through mechanical mixing into liquid monomers of thermosetting polymer, constituted

by the bisphenol A diglycidyl ether (DGEBA). A mold is then filled with the liquid composite. The mold is put into a vacuum oven in order to remove bubbles deriving from the mixing process. After opening the vacuum valve, adequate intervals of time and temperature permit the in situ polymerization and the curing process in order to obtain cross-linked thermosetting polymer, charged with the filler.

Table 2 resumes the main energy requirements assumptions for the epoxy composite production. In particular, it integrates the data already depicted in Fig. 2. As mentioned before for the GnP production process, further data concerning the raw materials extraction and preparation are included in the Ecoinvent modules used in this study.

2.4 Life cycle inventory—waste management

The waste management stage includes the end-of-life treatment of the epoxy resin. The question of how to dispose of end-of-life thermoset composite parts is growing in importance, in order to find more sustainable solutions (Jacob 2011). Although an intense research activity is ongoing in order to improve the current thermosets' recycling processes (Pickering 2006), the disposal of epoxy resins is still mostly characterized by either landfill or incineration. Actually, landfill and incineration have always been the simplest and
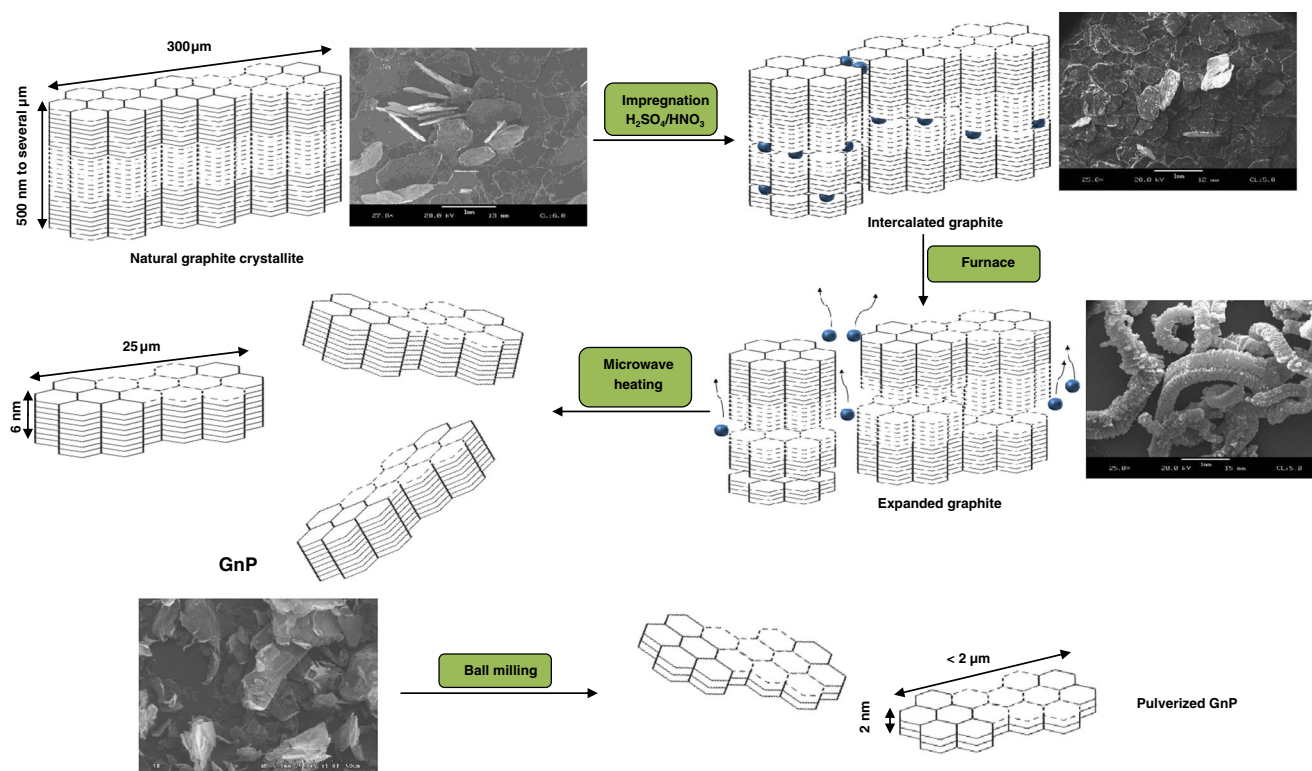

Fig. 3 Steps of GnP production process. The images of natural graphite flakes, intercalated (expandable) graphite and after heat affected exfoliation/ expansion graphite are reproduced with permission from A. Tamashausky, Director of Technical Service (Asbury Carbons)

Table 2 Summary of the inventory data (nanowastes and nanoemissions were not considered by lack of robust inventory)

Life cycle phase: Raw materials extraction and filler and resin preparation			
Characteristics	Unit	Adopted value	Ecoinvent module used
Natural graphite flakes[1]	kg	0.0580	Graphite, at plant/RER U
+ Transport	kg km	1,102	Transport, barge tanker/RERU
+ Transport	kg km	58	Transport, lorry >32 t, EURO5/RER U
H_2SO_4 95 %[2]	kg	0.1547	Sulfuric acid, liquid, at plant/RER U
+ Transport	kg km	154.7	Transport, lorry >32 t, EURO5/RER U
HNO_3 62 %[2]	kg	0.0770	Nitric acid, 50 % in H_2O at plant/RER U
+ Transport	kg km	77	Transport, lorry >32 t, EURO5/RER U
Energy consumption (water drying)[3]	MJ	0.0533	Electricity, production mix UCTE/UCTE U
Energy consumption (microwave heating)[4]	W h	9,250	Electricity, production mix UCTE/UCTE U
Energy consumption (ball milling)[5]	W h	40.95	Milling, cast iron, small parts/RER U
+ Transport (GnP to Composite Production)	kg km	0.0580	Transport, lorry >32 t, EURO5/RER U
Phthalic anhydride[6]	kg	0.4187	Phthalic anhydride, at plant/RER U
+ Transport	kg km	418.7	Transport, lorry >32 t, EURO5/RER U
DGEBA[6]	kg	0.5233	Epoxy resin, liquid, at plant/RER U
+ Transport	kg km	523.3	Transport, lorry >32 t, EURO5/RER U
Life cycle phase: composite production			
Characteristics	Unit	Adopted value	Ecoinvent module used
Energy consumption (mechanical mixing)[7]	W h	667	Electricity, production mix UCTE/UCTE U
Energy consumption (outgas in vacuum)[8]	kJ	47.96	Electricity, production mix UCTE/UCTE U
Energy consumption (curing)[8]	kJ	109.62	Electricity, production mix UCTE/UCTE U
Life cycle phase: distribution			
Characteristics	Unit	Adopted value	Ecoinvent module used
Composite distribution	kg km	1,000	Transport, lorry >32 t, EURO5/RER U
Life Cycle Phase: End-of-life			
Characteristics	Unit	Adopted values	Ecoinvent module used
Waste management	kg	1	Waste scenario/FR U
Transport	kg km	1,000	Transport, lorry >32 t, EURO5/RER U

[1] 5.8 wt% of the expanded exfoliated graphite was added into the epoxy system (Drazl and Fukushima 2009)

[2] Natural graphite was impregnated into an acid mixture of 95 % sulfuric acid and 62 % nitric acid, with respect to mass ratio proposed by Kwon et al. (2001)

[3] In the case of industrial dryer for mass production, convective or direct drying is considered. Typical values for spray drying for mass energy consumption (MEC) are 2.5 to 9 MJ/kg of water vaporized. The value adopted was 5 MJ/kg

[4] Graphite expansion by application of microwave energy at 2.45 GHz (Drazl and Fukushima 2009), for 5 min and then for 3 h, considering a power consumption of 1,000 W (ADEME 2006) and an output power efficiency of 30 %

[5] Data taken from Ecoinvent (2010) module "Milling, cast iron, small parts/RER U"

[6] A mass ratio curing agent (phthalic anhydride)/DGEBA = 0.8 was considered

[7] Mechanical mixing for 20 min, power consumption of 2,000 W

[8] Energy calculated with the assumption of an adiabatic oven

preferred methods of disposal accounting for 98 % of composite waste, while alternative routes such as re-use and mechanical recycling account for the remaining 2 % (Halliweel 2006). The traditional disposal routes, however, are becoming increasingly restricted. On the one hand, landfill is a relatively cheap method, but it is the least preferred waste management option under the European Union Waste Framework Directive. On the other hand, incineration is another common method, but around 50 % of the composite waste remains as ash, and this has to be landfilled (Jacob 2011). An important aspect that should be considered and that makes the recovery of thermosetting polymer parts complex

and expensive derives from the characteristics of nanocomposites themselves. Composite materials are made of two or more constituent elements with significantly different properties, that, when combined, produce a final material with different characteristics from those of individual components. To improve the properties of the composite, the combination (interfaces or interphases) needs improvement. The idea to prepare nanocomposites with large interfaces has thereby emerged. The drawback is that the more the constituents are combined, the more they are difficult to separate. In this study, the Ecoinvent waste French scenario (*Waste scenario/FR U*) was used despite the fact that this scenario is not formally applicable to recycling of epoxy resins. To do so, a specific module was created based on the Waste scenario/FR U but in which all the recycling was excluded for any materials and only incineration 53 % and landfill 47 % were kept. It is pertinent as our composite contains carbon nanofillers which prevent any recycling due to possible nanotoxicity. A change of the ratio between incineration and landfill ranging from 100 to 0 % still does not affect the conclusion of the present LCA: the end-of-life phase remains always the phase which impacts the least.

3 Life cycle impact assessment results

3.1 Process contributions

The result of the LCIA for GnP epoxy composite, from cradle to grave, is illustrated in Table 3 and Fig. 4. In particular, the process contribution describes in detail which processes contribute to the potential impacts. The potential impacts are summarized in the four life cycle phases: raw materials

extraction and filler and resin preparation; production of the epoxy GnP nanocomposite; distribution; and end-of-life. From Table 3 and Fig. 4, it appears that the raw materials extraction and filler and resin preparation phase have the highest contribution. Using the whole system boundary, the life cycle CED for the epoxy nanocomposite is 308 MJ/kg, and the total CO_2 equivalent emission is 16 $kgCO_{2\ eq}$. The contribution from the first phase to GWP and to the energy consumption (see Table 4) corresponds respectively to 92 and 96 % of the total impact. Figure 4 also shows that the waste management has an important impact on the *Ecotoxicity—USEtox* category.

Furthermore, Table 5 shows details concerning the most impacting phase. In particular, energy contributions in terms of primary energy related to the nanofiller, the curing agent, and the polymer matrix (which includes liquid monomers of thermosetting polymer) are reported. Table 6 describes energy requirements in terms of primary energy for the GnP production process.

3.2 Sensitivity analysis

A sensitivity analysis is carried out on the electricity mix used during the GnP production process and composite production, in order to see the influence of this important assumption. In particular, the Swiss electricity mix (60 % hydro power + 40 % nuclear) was used, in comparison to UCTE mix. It is well known that the CO_2-equivalent emissions vary drastically for different electricity mixes. Figure 5 compares energy consumption and GWP 100a indicators for both electricity scenarios. It appears that when switching to Swiss electricity, the raw materials extraction and filler and resin preparation are still the most impacting phase.

Table 3 Summary of the life cycle impact assessment from cradle to grave for 1 kg epoxy nanocomposite

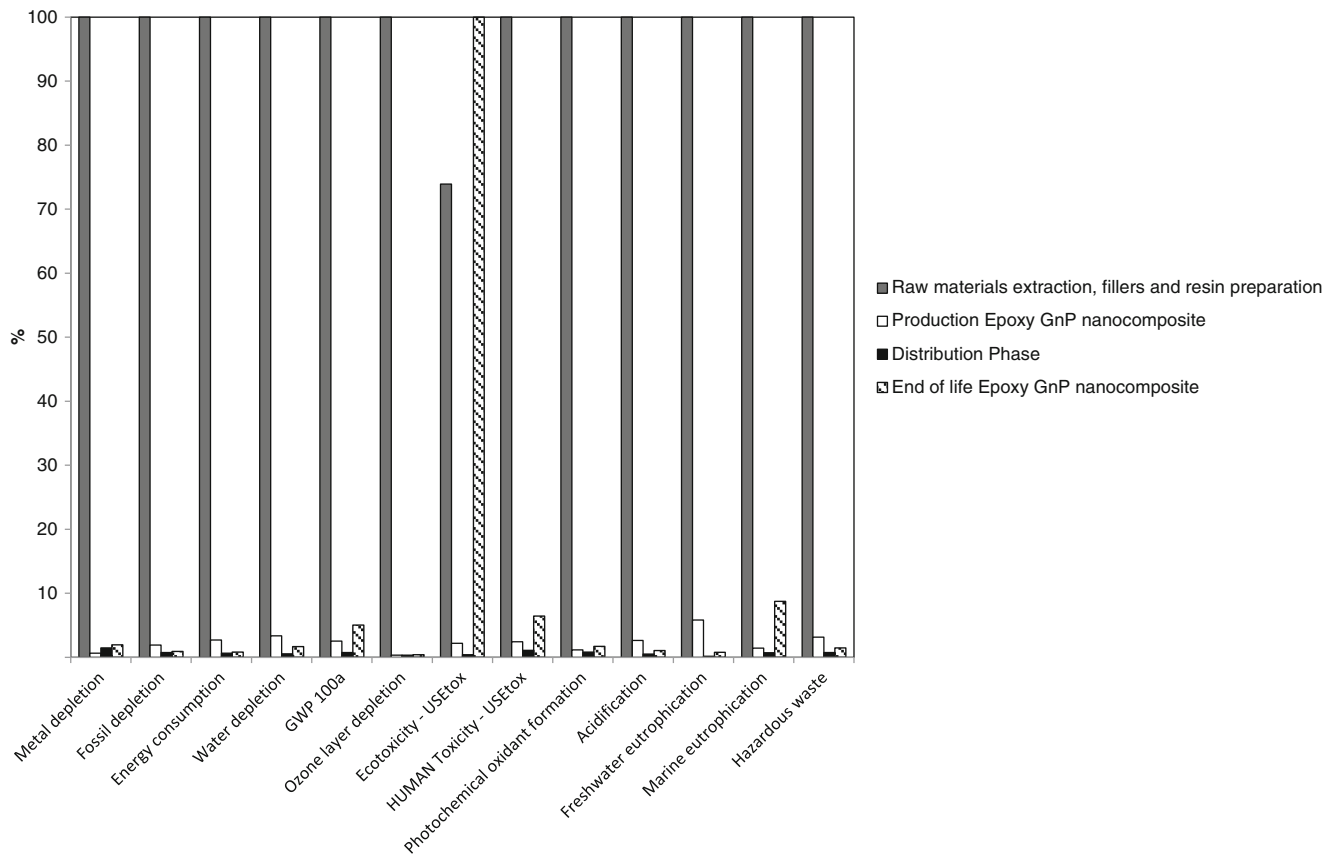| Impact category	Unit	Total	Raw materials extraction and filler and resin preparation	Production epoxy nanocomposite	Distribution	End-of-life
Metal depletion	kg Fe eq	4.31E-01	4.14E-01	2.62E-03	6.03E-03	8.00E-03
Fossil depletion	kg oil eq	5.82E+00	5.63E+00	1.07E-01	4.10E-02	5.08E-02
Energy consumption	MJ primary	3.08E+02	2.96E+02	7.92E+00	1.84E+00	2.37E+00
Water depletion	m³	9.46E-02	8.97E-02	2.99E-03	4.71E-04	1.48E-03
GWP 100a	kg CO_2 eq	1.57E+01	1.45E+01	3.67E-01	1.07E-01	7.25E-01
Ozone layer depletion	kg CFC-11 eq	5.64E-06	5.58E-06	1.81E-08	1.76E-08	2.14E-08
Ecotoxicity—USEtox	PAF m³ day	2.11E+02	8.84E+01	2.63E+00	4.68E-01	1.20E+02
Human toxicity—USEtox	CASES	4.16E-06	3.78E-06	9.10E-08	4.15E-08	2.43E-07
Photochemical oxidant formation	kg NMVOC	6.86E-02	6.62E-02	7.68E-04	5.33E-04	1.13E-03
Acidification	kg SO_2 eq	6.97E-02	6.69E-02	1.75E-03	3.36E-04	7.12E-04
Freshwater eutrophication	kg P eq	6.64E-03	6.22E-03	3.62E-04	1.07E-05	4.78E-05
Marine eutrophication	kg N eq	2.46E-02	2.22E-02	3.15E-04	1.53E-04	1.94E-03
Hazardous waste	kg	2.73E-04	2.59E-04	8.14E-06	1.89E-06	3.80E-06

Fig. 4 Graphical summary of the life cycle impact assessment from cradle to grave for 1 kg epoxy nanocomposite

3.3 Uncertainty analysis—Monte Carlo analysis

In general, LCA data is full of uncertain numbers. These uncertainties can have different causes, such as uncertain measurements, or uncertainty about how representative a figure is for the studied problem. It is fundamental to analyze how certain or uncertain the results are. Monte Carlo analysis is a numerical way to process uncertainty data and establish an uncertainty range in the calculation results. This technique was performed in SimaPro for the GnP production step and for the entire life cycle of the epoxy composite. In particular, a confidence interval of 95 % and a fixed number of runs (10,000) were applied. Figures 6 and 7 show, for each impact

category, a bar chart with an uncertainty range. The range expresses the 95 % confidence interval. This means that 95 % of the results lay within this range.

4 Interpretation and discussion

From Tables 3 and 4, it is clear that *raw materials extraction and filler and resin preparation* phase have the highest impact potential. However, as shown in Table 5, the GnP production process contributes in this phase for 36 %, while 50 % of the primary energy demand is covered by the matrix polymer constituent, DGEBA. In this sense, the matrix of epoxy

Table 4 Process contribution analysis for the impact categories Global Warming Potential 100a and energy consumption (CED)

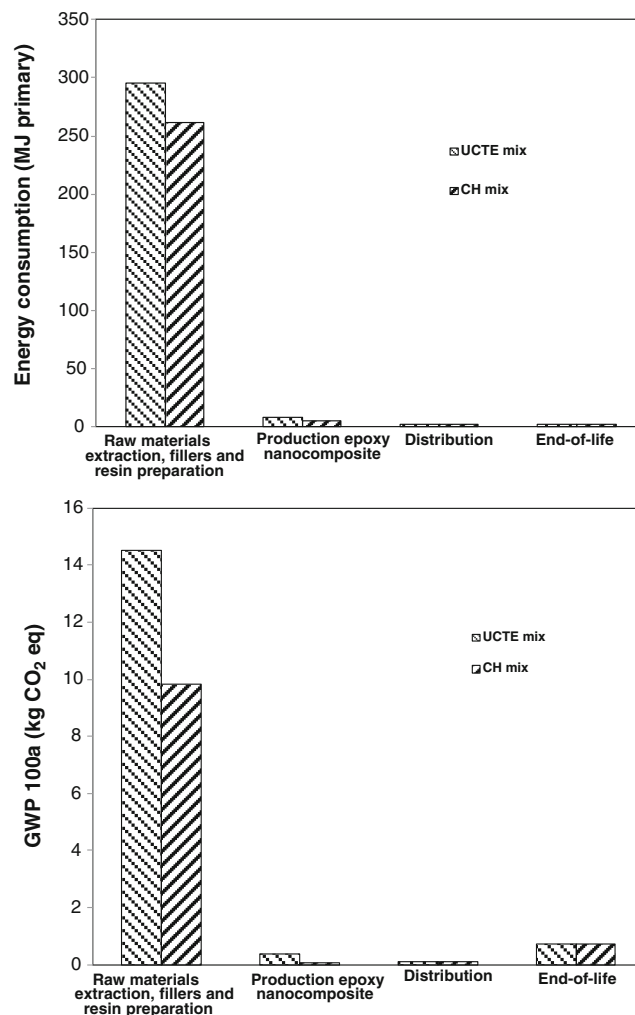| Life cycle stage	GWP 100a (kg CO$_2$ eq)	Percentage of total impact	Energy consumption (MJ primary)	Percentage of total impact
Raw materials extraction and filler and resin preparation	14.5	92.34	296	96.05
Production epoxy nanocomposite	0.367	2.34	7.92	2.57
Distribution	0.107	0.68	1.84	0.60
End-of-life	0.725	4.63	2.37	0.77
Total	15.7	100	308	100

Table 5 Energy contributions for 1 kg epoxy nanocomposite at plant

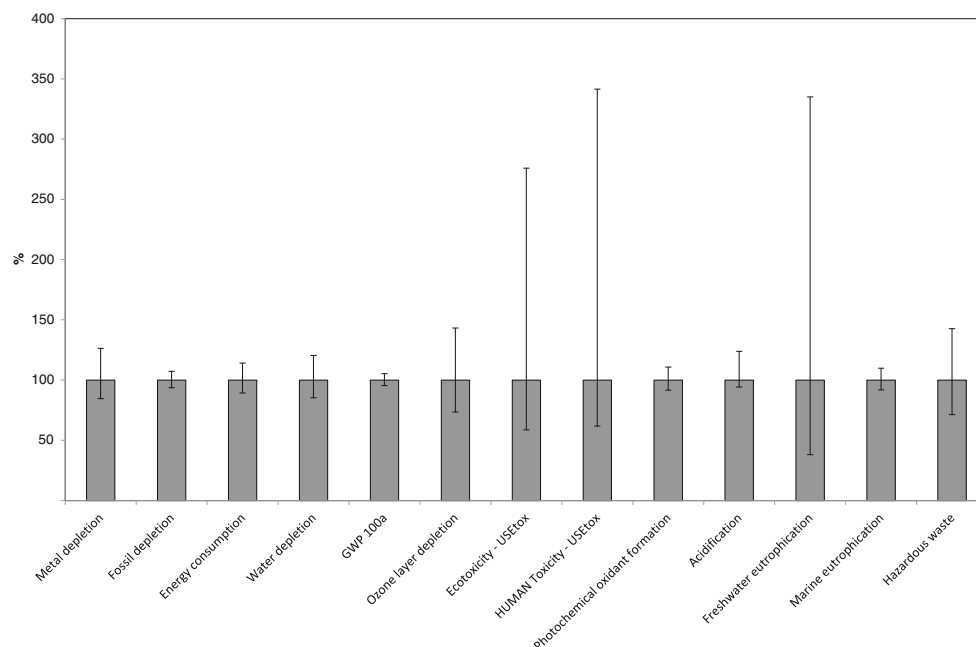| Characteristics			Unit	Value	Percentage of total energy impact
Raw materials extraction and filler and matrix preparation	GnP production	Filler	MJ primary	109	35.97
	Phthalic anhydride		MJ primary	33.7	11.10
	DGEBA	Matrix	MJ primary	153	50.32
Production epoxy nanocomposite			MJ primary	7.92	2.61
Total			MJ primary	303	100

composite appears to be more impacting than the filler. Deeper studies should be conducted in order to investigate a more environmental compatible material. It is worth remembering that the raw materials for epoxy resin production are largely petroleum-derived. An alternative route is based on the conversion of glycerin, as renewable feedstock, to produce epichlorohydrin, involved with bisphenol A in the production of DGEBA. Recently, glycerin has become increasingly available as a by-product of the manufacture of biodiesel, particularly in Europe. Its price has declined to a point where its use in the manufacture of commodity chemicals, such as epichlorohydrin, has become feasible (Bell et al. 2008). Glycerin-based epoxy resins express in almost all environmental categories less impact than propylene-based ones (Kočí and Loubal 2012). Concerning the GnP production, Table 6 depicts that the second step of microwave heating has significant impact (92 %) on the total primary energy, due to the microwave power and duration. This step results, as mentioned before, necessary for sufficiently long time to break down the expanded graphite.

An in-depth study was conducted on SimaPro, analyzing only the end-of-life phase, in order to investigate the presence of a particular substance responsible for the prevalence of the end-of-life in the *Ecotoxicity* impact category. Firstly, it appears that the French waste scenario is predominant compared to the transport considered in this phase. Secondly, studying the characterization step for the *Ecotoxicity—USEtox*

category, copper and zinc ions result to have particular impact roles in water emissions. In fact, these elements have been found as raw material in the inventory of the products used for the preparation of epoxy composite. The toxic effects of copper on numerous aquatic flora and fauna have been studied intensely over several years. In general, there is a consensus that the free cupric ions are more toxic if compared with other chemical forms such as organic copper complexes (Nor 1987).
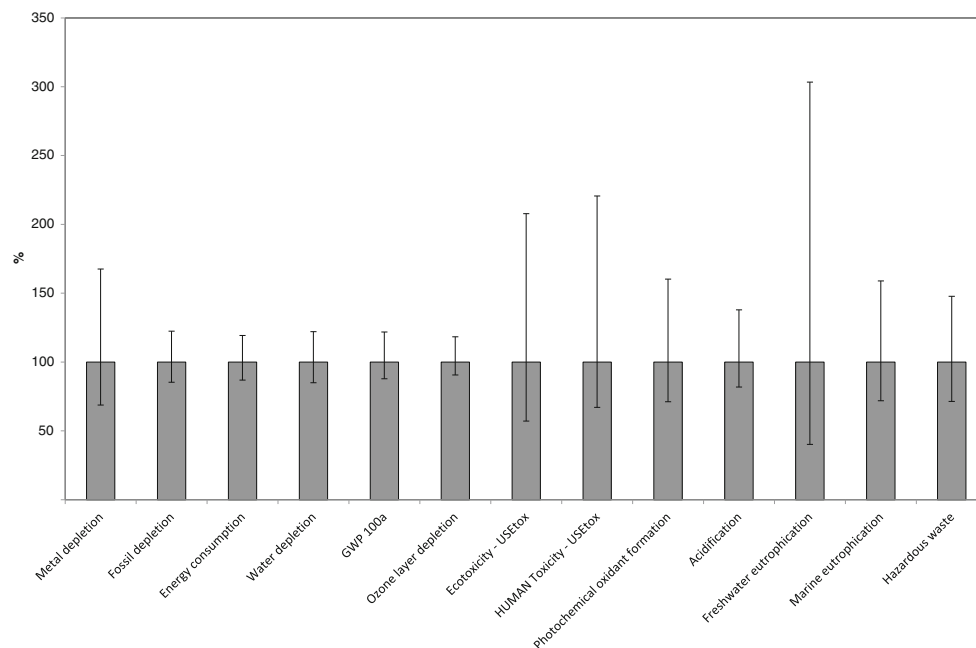
Table 6 Energy contributions for GnP at plant

Characteristics	Unit	Value	Percentage of total energy impact
Graphite	MJ primary	0.798	0.73
H_2SO_4	MJ primary	0.613	0.56
HNO_3	MJ primary	1.17	1.07
Water drying	MJ primary	0.165	0.15
Microwave I	MJ primary	2.79	2.55
Microwave II	MJ primary	100	91.95
Milling	MJ primary	3.14	2.88
Transport	MJ primary	0.107	0.10
Total	MJ primary	109	100

Fig. 5 Influence of a change in the electricity mix during the life cycle assessment of 1 kg epoxy nanocomposite

Fig. 6 Monte Carlo analysis for GnP production process

The sensitivity analysis is aimed to test the robustness of the results, studying relationships between input and output variables. Many factors, such as the transportation distances and graphite synthesis methods, could affect the environmental impact results. However, it is clear that the electricity used during the filler preparation and composite production is by far the most impacting element. It is worth noting that a change in the electricity mix (from UCTE to Swiss mix) does not affect the conclusions: the filler and resin preparation phase remains the most impacting phase.

Concerning the Monte Carlo analysis, Figs. 6 and 7 show the graphical comparison of the uncertainty range of individual impact categories. According to the results, the impacts of ecotoxicity, human toxicity, and freshwater eutrophication can vary greatly when the uncertainties of LCI and LCIA procedures are considered. This is mainly caused by a lack of consensus on these environmental aspects, their associated values and measurements. However, the GWP 100a and energy consumption, two important indicators especially nowadays that there is a very large interest in carbon dioxide

Fig. 7 Monte Carlo analysis for GnP epoxy composite life cycle

emissions and primary energy efficient production and consumption, exhibit lower dispersion of results.

5 Conclusions

The focus of this work has been to assess the environmental impacts of the life cycle of epoxy resins as nanocomposites filled with GnP. Among the four life cycle phases considered (raw materials extraction and filler and resin preparation; production of epoxy nanocomposite; distribution; end-of-life), the first is unambiguously found to be the most impacting phase. The composite production is negligible compared to the filler and epoxy matrix preparation. The matrix of the composite appears to be the most impacting material on the whole life of the nanocomposites, which moreover cannot be easily reformed or recycled.

In particular, the key numerical results obtained are the following: 1 kg of GnP filler requires 1,879 MJ of primary energy to be produced while the preparation of 1 kg of epoxy composite loaded with 0.058 kg of GnP 303 MJ; and the primary energy required to make epoxy resin is 187 MJ, i.e., 62 % of the total energy to make 1 kg of composite. Further investigations on a less impacting matrix material and a comparative analysis with other nanofillers have to be conducted, always considering not only the impacts assessment but also the final properties achieved with these fillers. Despite the fact that epoxy composites will remain energy-intensive materials to make, specific studies that consider the use phases could show that high energy requirements might be counterbalanced by energy-saving properties in some applications, such as aeronautic or aerospace.

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